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COMPARATIVE STUDY OF PbS-NiO AND NiO-PbS HETEROJUNCTION THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION TECHNIQUE

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Using chemical bath deposition technique, ternary stack thin films of PbS-NiO and NiO-PbS were deposited on plane glass substrates at bath temperature of 80^0C. Both heterojunction films were subjected to 300-1000nm range spectrophotometric analysis, which provided the absorbance data from which the transmittance and other optical constants were estimated. Structural characterization were also done on these films using X-ray diffraction which clearly showed similar diffraction patterns and peaks for both heterojunction film deposits. The surface morphology of the films were investigated with scanning electron microscope which showed different patterns and distribution of grain sizes. The band gaps of the films were affected differently by parametric variation of annealing temperature. It decreased with annealing temperature for PbS/NiO films whereas NiO/PbS thin films showed increase in band gap with annealing temperature. Direct band gaps of 1.88eV, 1.55eV and 1.30eV were obtained for PbS/NiO films for as-deposited, thermally annealed at 473K and 673K respectively while that of NiO/PbS films are 1.38eV, 1.63eV and 2.38eV for as-deposited, thermally annealed at 473K and 673K respectively. It is seen that both heterojunction thin films differed in their band gaps thus providing tuning effect to the band-gap for special applications. The formation of PbS/NiO and NiO/PbS heterojunction thin films considerably modified the optical properties of the independent films.

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Keywords: Absorbance, Transmittance, Chemical bath, Heterojunction, Bandgap

1. Introduction

Thin films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors, supercapacitors, etc. Core-shell structured materials have been receiving extensive attention because of their various applications such as coatings, solar cells and photocatalysis [1]. The shell can alter the charge, functionality, and reactivity of surface, or improve the stability and dispersive ability [2]. Furthermore, catalytic, optical, or magnetic functions can be imparted to the core particles by the shell material [2]. In general, the synthesis of core/shell structured material has the goal of obtaining a new composite material having synergetic or complementary behaviours between the core and shell materials [2]. There are many studies on the synthesis of core-shell thin films. Deposition of core-shell thin films by thermal evaporation [3], spin coating [4-5], sputtering [6-8], sol-gel [9-11], chemical vapour deposition [12-14] and chemical bath deposition [15-19] have been reported. The chemical deposition route is attracting considerable attention as it is relatively inexpensive, simple and convenient for large area deposition. It is a slow process which facilitates better orientation of

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crystallites with improved grain structure [20]. Depending upon the deposition conditions such as the bath temperature, stirring rate, pH, solution concentration, etc., the film growth can take place by ion-by-ion condensation on the substrates or by adsorption of the colloidal particles from the solution onto a substrate [20]. Economic considerations, simplicity and availability of raw materials are the basis for large area thin films deposition by chemical deposition techniques. It does not require sophisticated instrumentation like vacuum systems and other expensive equipment. Unlike in ED, electrical conductivity of the substrate is not a necessary requirement in chemical deposition. Hence, any insoluble surface to which the solution has free access will be a suitable substrate for deposition [21]. In this present work, we contribute by successfully depositing PbS/NiO and NiO/PbS core-shell thin films using chemical bath deposition technique, with emphasis on the structural, morphological and optical properties of the deposited films.

2. Experimental

Chemical bath deposition technique was used to fabricate heterojunction thin films of PbS/NiO and NiO/PbS on plane glass substrates. The substrates were plane glass slides of 75 x 25 x $1mm^3$ dimension which were previously degreased in concentrated hydrochloric acid, washed in detergent solutions, rinsed with distilled water and left to dry in dust-free environment. First, PbS film was deposited by mixing 5ml of 0.2M $Pb(NO_3)_2$, 5ml of 1M $SC(NH_2)_2$, 5ml of IM NaoH, and 35ml distilled water in a 50ml beaker, these contents being vigorously stirred. The substrates were vertically inserted in the solution and suspended from a synthetic foam which rests on top of the beaker. The bath was left for 50 minutes at room temperature, after which the glass slides covered with dark PbS deposits were removed, rinsed in distilled water and left to drip-dry in dust-free air. To deposit PbS/NiO films, PbS film already deposited was inserted into a bath containing 10ml of 0.2M $NiSO_4$, 5ml of 100% NH_3 and 27ml of water into 50ml beaker with the mixture being vigorously stirred into homogenous solution. The deposition of NiO/PbS films was achieved by dipping NiO deposits into a mixture containing 5ml of 0.2M $Pb(NO_3)_2$, 5ml of 1M $SC(NH_2)_2$, 5ml of IM NaoH, and 35ml distilled water in a 50ml beaker. Thermo scientific GENESYS 10S model UV-VIS spectrophotometer on the 300-1000 nm range of light at normal incidence to samples was used to obtain the absorbance data from which transmittance, absorption coefficient and other optical constants were determined. Structural characterizations were also done on the deposited films using the Rigaku Ultima IV X-ray diffractometer equipped with a graphite-monochromated CuK_α radiation source (40KV, 30mA) of $\lambda = 0.15406nm$ to scan continuously as 2θ varies from $0 – 100^o$ at a step size of 0.034^0 and at a scan step time of 57.6s.

3. Results and discussion

3.1. Elemental composition analysis

The elemental composition analysis of the deposited films were probed by high energetic Rutherford backscattering (RBS) by Proton Induced X-ray Emission (PIXE) scans on the samples from a Tandem Accelerator Model 55DH 1.7MV Pellaton. The RBS micrographs depicting the various elements in the film samples as well as the glass substrate are shown in figures 1 and 2 for PbS-NiO and NiO-PbS core-shell thin films respectively while the percentage elemental compositions are shown in table 1 and 2 for PbS/NiO and NiO/PbS thin films respectively.

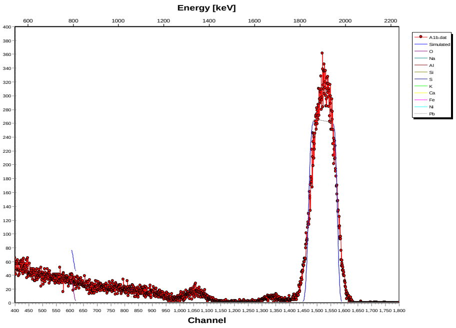


Fig. 1. Showing RBS micro graph of PbS/NiO thin film

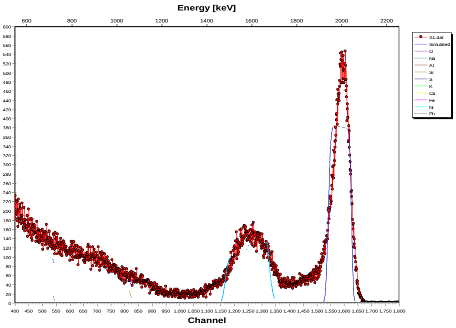


Fig. 2. Showing RBS micro graph of NiO/PbS thin film

Table 1. % composition of PbS/NiO films

Sample	Pb	Ni	Fe	Ca	K	S	Si	Al	Na	O
Glass Slide	-	0.30	0.30	6.00	3.50	-	34.00	5.20	25.00	26.00
PbS/NiO	8.11	1.10	-	-	-	2.78	-	-	-	95.55

Table 2. % composition of NiO/PbS films

Sample	Pb	Ni	Fe	Ca	K	S	Si	Al	Na	O
Glass Slide	-	-	0.30	6.00	3.50	-	34.00	5.20	25.00	26.00
NiO/PbS	22.44	65.32	-	-	-	12.25	-	-	-	71.24

The RBS results clearly indicate that all the essential elements (Pb, Ni, S, O) that make up the films were present. The thicknesses of PbS/NiO and NiO/PbS thin films as deciphered by RBS are 694.00nm and 416.3nm respectively.

3.2. Structural Studies

The results of the XRD scan done on PbS/NiO and NiO/PbS stacks are shown in Figures 3 and 4 respectively. Similar diffraction peaks can be observed for both film deposits. PbS film sample showed prominent peaks at 2θ values of approximately 26^o and 30^o which are associated with the (111) and (200) planes with JCPDS Card No. 00-005-0592 whereas NiO film sample showed prominent peaks at 43^o and 63^o corresponding to the (200) and (220) planes with JCPDS Card No. 00-047-1049 of Bunsenite phase. The sharp and multiple peaks indicate that both films are polycrystalline in nature.

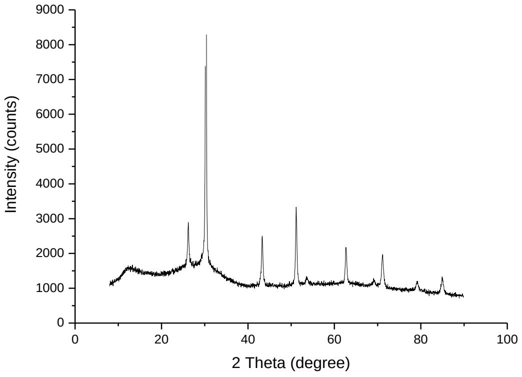


Fig. 3. XRD pattern of PbS-NiO

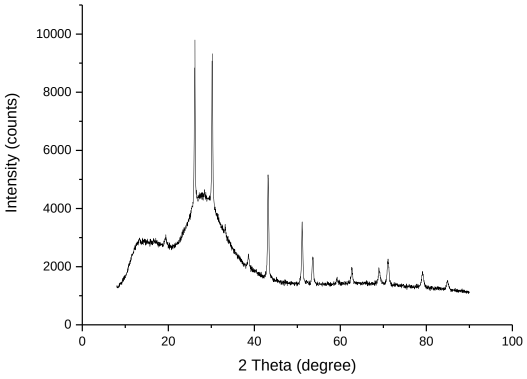
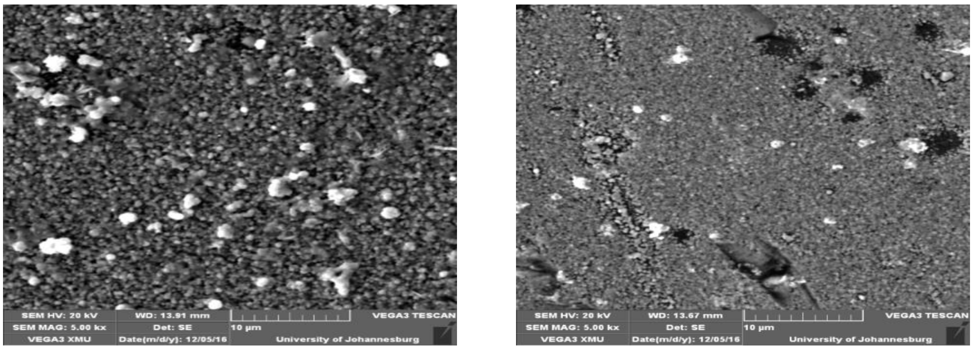


Fig. 4. XRD pattern of NiO-PbS

3.3. Morphological Studies

Fig. 5a-b show the SEM images of the PbS-NiO and NiO-PbS deposits prepared at same conditions. It is clearly seen that the morphology of the PbS-NiO films differ significantly from that of NiO-PbS films. PbS-NiO deposit consists of densely packed structure when compared to NiO-PbS films.



(a) *(b)*

Fig. 5. SEM images of (a) PbS-NiO (b) NiO-PbS thin films

3.4 Optical properties

Figs. 6 and 7 show the absorbance, A and transmittance, T spectra of the stack quaternary PbS/NiO and NiO/PbS thin films. All the film samples showed high absorbance in the UV and visible regions dwindling with wavelength in the near infrared region. Maximum absorbance of 4 was observed for both films which is beyond the maximum stipulated by Lambert-Beer's law. The properties of high absorbance suggest that the films may be need as coating materials on the surface of solar collectors for enhanced solar energy collection. Both films generally have low transmittance in the UV-Visible regions with substantial increase in the NIR region. However, PbS/NiO films showed better transmission in the NIR region compare to NiO/PbS films in the same region. The low transmittance recorded by the films could be attributed to high concentration of the absorbing species. At high concentrations, particles collision increases leading to the trapping or absorption of light thereby reducing the transmission of light as it passes through the film samples. The transmittance of thin films can be greatly modified by different deposition parameters. In the literature, the concentration dependent optical behaviour and variation of transmittance caused by different deposition time have been reported [22, 23]. The properties of low transmittance in the UV and high transmittance in the NIR thin films make the films good materials for thermal control coatings inside buildings. The characteristics of low transmittance means that the film could also be suitable as filters in optical switching devices and also as dielectric materials.

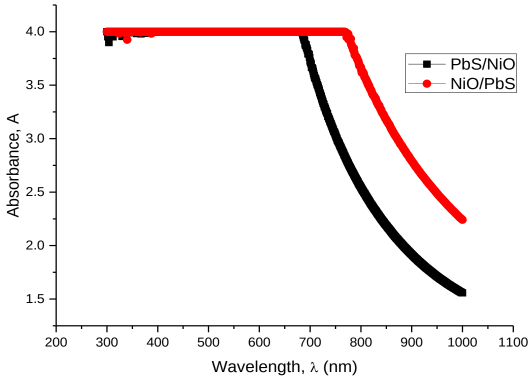


Fig. 6: Absorbance versus wavelength for the deposited stacks

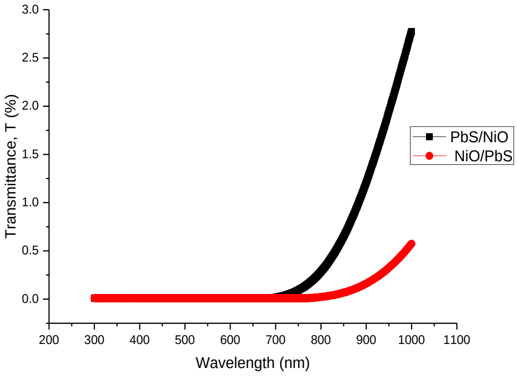


Fig. 7. Transmittance versus wavelength of the deposited stacks

The absorption coefficients, α is related to absorbance, A using lambert-Beer law [24].

$$\alpha = \frac{2.3026 \times \mathrm{A}}{t} \tag{1}$$

α was calculated for each thin film sample and shown in Fig. 8. Values for NiO/PbS are generally higher than those of PbS/NiO in the entire spectrum. This absorption coefficient, α is related to the energy gap, E_g of a semiconductor [25, 26].

$$\alpha hv = A(hv - E_g)^n \tag{2}$$

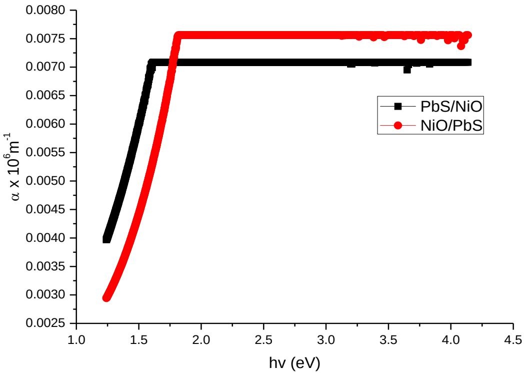


Fig. 8. Absorption coefficient as a function of photon energy

Where A is a constant, hv is the photon energy and α is the absorption coefficient. For direct allowed transition, n = ½ while for indirect ones, n = 2 or 3 depending on whether they are allowed or forbidden respectively. Hence a linear graph of $(\alpha hv)^2$ versus hv will show E_g as intercept on hv axis. Figure 9 reveals such direct energy gap of 1.88eV, 1.55eV and 1.30eV for as-deposited, thermally annealed at 473K and 673K respectively for PbS/NiO thin films. Fig. 10 reveals the direct band gap of NiO/PbS films as 1.38eV, 1.63eV and 2.38eV for as-deposited, thermally annealed at 473K and 673K respectively. Values for PbS, as widely reported is 0.34 – 0.37eV [27, 28] while that of NiO is 3.6-4.0eV [29, 30]. It can be seen that both stacks PbS/NiO and NiO/PbS shift the fundamental absorption edge of their binary origin, thus providing tuning effect to the band gap for special applications. The results also showed that the band gap of PbS/NiO and NiO/PbS thin films were affected differently by annealing temperature. The band gap of PbS/NiO films decreased with increase in annealing temperature while the band gap of NiO/PbS films increased with annealing temperature.

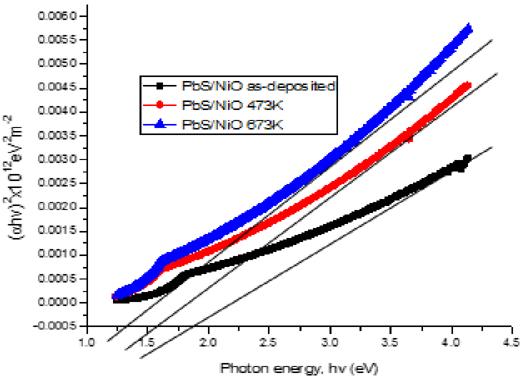


Fig. 9. $(\alpha hv)^2$ *as a function of hv for as-deposited, thermally annealed at 473K and 673K*

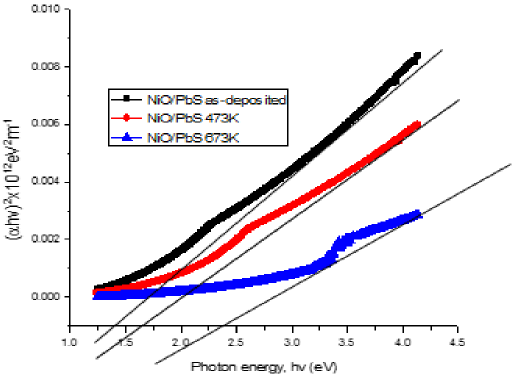


Fig. 10. Plot of $(\alpha hv)^2$ *as a function of hv for as-deposited, thermally annealed at 473K and 673K*

The band gap decreases of PbS/NiO films could be due to many body effects like the exchange energy due to electron-electron and electron-impurity interactions which occurs when the carrier density exceeds a certain value and causes narrowing (red shift) of the band gap energy [31]. The decrease in the band gap of PbS-NiO films with annealing temperature could also be explained on the basis of quantum confinement effect which has two consequences: First it splits the conduction band into discrete levels and secondly, it reduces the density of states available in the conduction band such that at 673K, the carrier concentration gets to its critical value leading to the collapse of the potential barrier at the grain boundaries and hence abrupt decrease in the band gap at 673K. The decrease in band gap could also be due to the increase in crystalline size associated with increase in annealing temperature while the increase in band gap of NiO/PbS films with annealing temperatures could be attributed to the Burstein-Moss shift which occurs when the electron carrier concentration exceeds the conduction band edge density of states [32].

4. Conclusions

Chemical bath deposition technique was applicable in growing stack heterojunction thin films of PbS/NiO and NiO/PbS. Transmittance spectra of both stacks showed PbS/NiO films transmitting higher than NiO/PbS films for most frequencies.

Both are semiconductors but with different band gaps. Heat treatment of both films showed that the band gap of PbS/NiO films decreased with annealing temperature while that of NiO/PbS films increased with annealing temperature. The band-gap tuning from its binary film origin offer it for several new applications, such as in solar thermal application, selective surfaces and optoelectronic devices.

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